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by

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16. ABSTRACT An aerosol characterization, visibility, and receptor modeling study was conducted in the Shenandoah Valley, VA between July 14 and August 15, 1980. The objectives of this study were to: (1) determine the origin of the ambient particles, (2) determine the major chemical species contributing to the light extinction coefficient, (3) evaluate analytical methods to characterize aerosols, and (4) provide data for comparison with chemical composition of aerosols collected in the Great Smoky Mountains and in the Abastumani Mountains of Georgian Soviet Socialist Republic. The average sulfate concentrations measured at these three locations were: Great Smoky Mountains, 12.0 μg m^{-3}; Shenandoah Valley, 13.6 μg m^{-3}, and Abastumani Mountains, 4.5 μg m^{-3}. For the two studies in the United States, the fine particle sulfate during sulfate maxima was mostly in the form of ammonium acid sulfate. Factor analysis modeling of the fine aerosol composition measured in the Shenandoah Valley yielded a persistent factor containing large loadings on mass, $SO_4^=$, S, NH_4^+, H^+, Se, and total nitrate (sum of particulate nitrate and nitric acid), which is characteristic of coal-fired sources. The factor analysis grouping along with additional supporting analytical data suggests the identity of emission sources contributing the fine and coarse particles measured in the Shenandoah Valley. From the elemental composition of the fine particles and trajectory analysis, it is inferred that the sulfate's origin is mainly coal-fired power plants.

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SOURCE APPORTIONMENT METHODS APPLIED TO THE DETERMINATION OF THE ORIGIN OF AMBIENT AEROSOLS THAT AFFECT VISIBILITY IN FORESTED AREAS

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Abstract: An aerosol characterization, visibility, and receptor modeling study was conducted in the Shenandoah Valley, VA between July 14 and August 15, 1980. The objectives of this study were to: (1) determine the origin of the ambient particles, (2) determine the major chemical species contributing to the light extinction coefficient, (3) evaluate analytical methods to characterize aerosols, and (4) provide data for comparison with chemical composition of aerosols collected in the Great Smoky Mountains and in the Abastumani Mountains of Georgian Soviet Socialist Republic. The average sulfate concentrations measured in fine particles (< 2.5 μm) at these three locations were: 12.0 μg m^{-3} at Great Smoky Mountains; 13.6 μg m^{-3} at Shenandoah Valley, and 4.6 μg m^{-3} at Abastumani Mountains; the fractions of sulfate in the fine particle mass concentrations at each site were 0.50, 0.50, and 0.38, respectively. For the two studies in the United States, the fine particle sulfate during sulfate maxima was mostly in the form of ammonium acid

sulfate. Factor analysis of the fine aerosol composition measured in the Shenandoah Valley yielded a persistent factor containing large loadings on mass, $SO_4^=$, S, NH_4^+, H^+, Se, and total nitrate (sum of particulate nitrate and nitric acid), which is characteristic of coal-fired sources. Such a factor analysis grouping along with additional emissions information suggests that the sulfate's and nitrate's origin is mainly coal-fired power plants.

INTRODUCTION

Ambient aerosol characterization studies conducted by Pierson et al. (1980), Weiss et al. (1977, 1982), Ferman et al. (1981), and Stevens et al. (1980) revealed that fine particle sulfate was the principal contributor to visibility degradation in rural forested areas in the eastern United States. These observations were in sharp contrast to the earlier speculations of Went (1960) and Rasmussen (1972), who concluded that organic emissions from trees and plants were the principal contributors to haze in remote forested areas. The aerosol characterization studies by Stevens et al. (1980) and Ferman et al. (1981) included measurements to infer the origin of the sulfate and carbon in the fine particles. Ferman et al. (1981) used back trajectory analysis to determine the origins of air masses passing over their Shenandoah Valley sampling site. They found that, when the sulfate concentration exceeded 10 μg m^{-3}, the air mass had passed over major industrial and urban source areas in the midwest. Trajectory analysis indicated that the air masses reaching the Great Smoky Mountains originated from a wide variety of directions and locations and did not originate from a single nearby source (Stevens et al., 1980).

In the Great Smoky Mountains study, terpenes were found to be a minor portion of the gas phase hydrocarbons. Stevens et al. (1980), therefore, concluded that terpene emissions from the pine trees did not appear to be significant contributors to ambient particulate carbon. This conclusion is supported by Altshuller (1983), who estimated that the 1 ppb C terpene concentrations observed in the Great Smoky Mountains (Arnts and Meeks, 1981) would produce between 0.1 and 0.2 $\mu g\ m^{-3}$ aerosol, which was a fraction of the aerosol carbon measured. Shaw et al. (1983), in studies conducted in the Abastumani Mountains, observed that, while terpenes often represented a significant portion of the gas and particle-phase hydrocarbons, they were a minor contributor to the fine particle mass.

In this paper the compositions of aerosol particles collected in the forested area of the Great Smoky Mountains and Shenandoah Valley and from the remote forested area of the Abastumani Mountains located in the Georgian Soviet Socialist Republic (SSR) are examined to determine if there exist any distinctive properties of particles peculiar to these areas to assist in source apportionment and visibility studies.

EXPERIMENTAL

Site Descriptions

Great Smoky Mountains Field Sampling Site: Measurements were made in a northern portion of the Great Smoky Mountains National Park near the Elkmont campground, at 35°40'N and 83°36'W. This location is 10 km southwest of Gatlinburg, TN, and 40 km southeast of Knoxville, TN. The site elevation at Elkmont is 646 m, and the elevation of mountain peaks located to the southeast and east is 2000 m. The site is surrounded on all sides by forest, which is a wilderness for 30 km to the south.

Abastumani Field Sampling Site: The Abastumani Astrophysical Observatory is about 200 km west of Tblisi, the capital of Soviet Georgia, and on the crest of Mt. Kanobili, 1700 m above sea level. The surrounding forests are dense and consist mainly of pine and fir. A small village lies in the valley to the east of the observatory. This site was chosen for a study of aerosols because of its distance from industrial areas, the expanses of coniferous forests which were expected to emit aerosol precursors, and the presence of the observatory to support an extended field study.

Shenandoah Valley Field Sampling Site: Figure 1 shows the location of the field sampling site in the Shenandoah Valley. The site is at an elevation of 275 m and is located in a large, recently-mowed field approximately 0.5 km from U.S. Highway 540. The Massanutten Mountain peaks located west of the sampling site, which were used in human and photographic studies of visual range, are depicted in an artist's rendering of the scenic view. The distances to the peaks were determined from U.S. Geological Service maps provided by the staff of U.S. National Park Service working at Shenandoah National Park. The site was selected by General Motors Research Laboratory personnel who generously allowed EPA and an EPA Grantee (U. Washington) to share the site and collect aerosol samples and visibility data simultaneously with the GM scientists.

Aerosol Sampling and Analysis

Table 1 is a list of the aerosol sampling equipment and collection conditions used to collect particles and shows the conditions under which field studies were conducted in the Great Smoky Mountains, Abastumani Mountains and Shenandoah Valley. Sampling duration was for most periods as cited in Table 1 except that (1) several 48-hour rather than 24-hour hi-vol

TABLE 1

Aerosol Sampling Equipment, Collection Conditions and Analyses Performed

Site/ Sampler	Filter Medium	Deposit Diam. mm	Flow Rate L min^{-1}	Sampling duration, h	Sampling periods	Aerosol Analysis
GREAT SMOKY MOUNTAINS						
Dichotomous	Teflon	30.5	52	12	12	mass, elemental
Dichotomous	Teflon	30.5	52	12	12	H^+, NH_4^+, NO_3^-, $SO_4^=$
Dichotomous	Quartz	29.5	16.7	24	12	carbon
ABASTUMANI MOUNTAINS						
Dichotomous	Teflon	29.5	16.7	12	40	mass, elemental
Dichotomous	Teflon	29.5	16.7	12	40	H^+, NH_4^+, NO_3^-, $SO_4^=$
Dichotomous	Quartz	29.5	16.7	12	40	carbon
Dichotomous	Nuclepore	29.5	16.7	12	40	mass, elemental
Hi-Volume	Quartz	a	1000	24	20	$^{14}C/^{12}C$
Micro-orifice Impactor	Teflon	29.5	30	12	14	mass, $SO_4^=$, NO_3^- particles of < 0.11 μm diameter
SHENANDOAH VALLEY						
Dichotomous	Teflon	29.5	16.7	12	28	mass, βabs, elemental
Dichotomous	Teflon	29.5	16.7	12	28	H^+, NH_4^+, NO_3^-, $SO_4^=$
Dichotomous	Quartz	29.5	16.7	12	28	carbon
Bell Vol	Quartz	a	500	24	12	$^{14}C/^{12}C$
Micro-orifice Impactor	Teflon	29.5	30	12	19	elemental
Fine NO_3^- + HNO_3	Nylon	2.5	7.6	12	26	total nitrate[b] (NO_3^- + HNO_3)

a A 20 x 25 cm quartz filter was used.

b Duplicate systems were used to collect fine nitrate samples.

samples were collected in Abastumani Mountains to obtain enough material for ^{14}C measurements, and (2) sampling was interrupted during rain storms in the Shenandoah Valley. More detailed descriptions of the experiments at Great Smoky Mountains and Abastumani are given by Stevens et al. (1980) and Dzubay et al. (1983), respectively.

Mass and Elemental Analysis: The mass measurements were made by β-ray attenuation with an instrument and procedure described by Jaklevic et al. (1981) and Courtney et al. (1982). The elemental concentration of aerosols collected were measured using an energy dispersive x-ray fluorescence (XRF) spectrometer (Jaklevic et al., 1976). The x-ray spectra were analyzed using a least squares fitting procedure (Drane et al., 1980). Calibration for sulfur was based upon pure ammonium sulfate aerosol deposits, which were analyzed gravimetrically and verified by wet chemical analysis (Shaw et al., 1980). For all analyzed elements except sulfur we used pairs of vapor-deposited metal films as standards (Micromatter Co., Eastsound, WA). Corrections for attenuation of soft x-rays in coarse particles were made with use of factors described previously (Dzubay and Nelson, 1975). A recent interlaboratory comparison (Dzubay et al, 1983) demonstrated that our measurements for elements having atomic numbers above 21 were consistent with mean values from eight laboratories within 0.5-10%. The uncertainties shown in Table 2 for the elements measured by x-ray fluorescence are the mean values of the uncertainties determined for each measured element. The sources of uncertainties in the XRF analyses include stability of the system, accuracy of the calibration standards, uncertainties in the attenuation corrections, and variabilities in counting statistics for each element.

Table 2. Comparison of Aerosol Analyses from Three Studies[a,b]

	Smoky Mountains Sept. 20-26, 1978		Shenandoah Valley July 23 - Aug. 5, 1980		Abastumani Mountains[c] July 3-24, 1979	
	Fine	Coarse	Fine	Coarse	Fine	Coarse
Mass	24000 ± 3000	5600 ± 3000	27000 ± 5000	7400 ± 5080	12220	5260
$SO_4^=$	12000 ± 1300	NA	13600 ± 1300	780 ± 200	4600	100
NO_3^- Particle	< 500	NA	306 ± 260	NA	< 400	190
NO_3^- Total	NA	NA	1271 ± 127	NA	< 600	NA
NH_4^+	2280 ± 390	NA	3356 ± 390	NA	1390	20
H^+	114	NA	96	NA	NA	NA
C Organic	2220 ± 400	1200 ± 400	440 ± 420	NA	1710	750
C Elemental	1100 ± 800	< 100	1120 ± 780	NA	980	110
C Total	3300 ± 600	1300 ± 600	1560 ± 660	1680	2690	960
Al	20 ± 18	195 ± 101	44 ± 35	311 ± 104	50	360
Si	38 ± 10	580 ± 262	116 ± 23	813 ± 288	200	940
S	3744 ± 218	204 ± 187	4539 ± 273	260 ± 237	1570	80
Cl	< 10	7 ± 4	10 ± 5	179 ± 63	5	30
K	40 ± 3	108 ± 30	61 ± 5	129 ± 30	130	100
Ca	16 ± 1	322 ± 73	35 ± 3	304 ± 54	80	330
Ti	< 6	18 ± 5	< 10	17 ± 10	< 10	9
V	< 4	< 5	< 10	< 10	NA	NA
Mn	NA	NA	3 ± 2	3 ± 2	187	38
Fe	28 ± 2	118 ± 9	54 ± 5	158 ± 12	70	200
Ni	1 ± 0.5	1 ± 0.5	1 ± 1	1 ± 1	< 1	< 1
Cu	3 ± 0.7	< 5	5 ± 2	6 ± 2	7	6
Zn	9 ± 1	< 4	11 ± 2	6 ± 2	15	6
As	2.2 ± 1	< 1	1 ± 1	< 2	< 1	0.3
Se	1.4 ± 0.3	0.2 ± 0.2	1.2 ± 0.5	< 1	< 1	< 1
Br	18 ± 1	5 ± 0.4	8 ± 1	3 ± 1	3	1
Pb	97 ± 5	14 ± 1	52 ± 4	9 ± 2	18	1

a) Results are expressed in units of ng m^{-3}; overall measurement errors are shown after the ± symbols.

b) The fine and coarse fractions pertain to particles having aerodynamic diameters in the ranges 0 to 2.5 and 2.5 to 15 μm, respectively.

c) The uncertainties for Mn are ± 10% of the concentration reported. The uncertainties in the other species are the same as those reported for the Shenandoah Valley.

NA - NOT ANALYZED

Nitrate Measurements: Nitrates measured in the Shenandoah Valley study were obtained from two sets of sampling systems. Samples collected on Teflon filters with dichotomous samplers every 12 hours immediately after sampling were placed into 30 ml polypropylene screw cap bottles containing 20 ml of 5×10^{-5} N perchloric acid solution. These solutions were stored at 5°C until they were analyzed by ion chromatographic and Grans titration procedures (Stevens et al. 1978). However, recent evaluation of methods of collecting and measuring nitrates (Stevens, 1979; Shaw et al., 1982) has shown that nitrates tend to evaporate from Teflon filters (negative artifact) during the sampling, resulting in erroneously low nitrate measurements. Therefore, in the Shenandoah Valley experiment, nitrates were also measured by sampling through a cyclone (Waggoner et al., 1981; Weiss, personal communication) which removed particles larger than 3.5 μm and by collecting fine-particle aerosol and nitric acid onto 25 mm diameter nylon filters with 1 μm pore size (Membrana Corp.). The sampling flow rate was 8.6 l min^{-1} and was maintained with a flow capillary restrictor. Sample duration was typically 12 hours. This sampling procedure collected both the fine particle nitrate and nitric acid on the same filter, and the two forms were not distinguished. Therefore, nitrate data from these measurements are referred to as total fine nitrate. Nitrates were extracted from the nylon filters and analyzed using the gas chromatographic procedure of Tesch et al. (1976). Based on simultaneous, duplicate measurements, the precision of the measurement was determined to be 10% or better with a confidence level of 95% (Smith et al., 1983).

Carbon and $^{14}C/^{12}C$ measurements: Volatile, elemental, and total carbon collected on quartz filters were determined by pyrolysis techniques. For all Bell-vol (Bell, 1982) and hi-vol samples, and for the dichotomous filter

samples collected at Shenandoah Valley, carbon was determined by a procedure described by Stevens et al. (1982). The dichotomous filter samples collected in the Abastumani Mountains were analyzed by a procedure described by Huntzicker et al. (1982). The carbon present in the samples collected in the Smoky Mountains was analyzed by another combustion procedure described by Johnson and Huntzicker (1979). The Bell-vol sampler was used in the Shenandoah Valley Study to collect fine particles on 20 x 25 cm Pallflex 2500 QAST quartz filters for subsequent ^{14}C analysis. The inlet consisted of six coaxial cylinders that provided a series of impaction surfaces to remove large particles. The upper 50% cutpoint was 4 ± 1 μm aerodynamic diameter. Sample filters and blanks were folded and wrapped in aluminum foil and stored in paper envelopes at room temperature.

After small portions of the 20 x 25 cm hi-vol and Bell-vol filters were removed for carbon analysis, the remaining portions were sent to National Bureau of Standards (NBS) for determination of $^{14}C/^{12}C$ ratios (Currie, 1982). During the Shenandoah Valley study the sampling site was infested with gnats. A few gnats were drawn into the Bell Vol sampler and portions (mainly wings and legs) were found on the filters. After the filters were returned to the laboratory, remnants of these insects were carefully removed from the filters with tweezers. A few small insects were also collected on the hi-vol filters used at Abastumani, and these were similarly removed before analysis. Inspection of the aerosols collected on quartz filters using the hi-vol sampler in Abastumani also revealed the presence of a few yellow granules, possibly pollen particles on most of the filters.

Size Distribution Measurements: To determine the size distribution of particles in the fine mode, samples were collected in a six-stage micro-orifice impactor developed by Kuhlmey et al. (1981). Each of the first five stages consisted of a thin plate having multiple round holes which served as jets that impacted aerosol onto a collection surface. The collection surface was a 2 μm pore size Teflon filter that was rotated continuously to cause particles to be deposited uniformly in concentric rings. The sequence of cutpoints for the impaction stages was 0.4, 0.4, 0.11, 0.11, and 0.3 μm. The last stage was used to test for particle bounce effects. In addition, a backup Teflon (1 μm) filter was used to collect particles not collected on the impactor stages, and a cyclone was used at the inlet of the device to remove particles larger than 2 μm. The backup filter and impactor stages were analyzed by β-gauge and XRF for mass, S, and Pb.

Visibility and Photographic Measurements (Shenandoah Valley): Each day during the study one visual range observation was made of the Massanutten Mountain peaks located south and west of our monitoring site (Fig. 1). These visibility measurements were made by human observers between 1045 and 1140 EST. Most of the observations were made at 1100 hrs. Simultaneously, color photographs of the same vista were taken using a Cannon A-35F Automatic camera with a 40mm/1:2.8 lens and Kodak ASA 400 color print film. The visual range estimates were based on the observer's knowledge of the distance to targets shown in Fig. 1. For example, on July 25, 1980 at 1100 hr, Duncan Knob was obscured by haze but Kennedy Peak was visible, and the haze partially obscured the valley between the two peaks. From this observation visual range was estimated to be 15 km. The color photographs taken at the time of the human observation served as excellent surrogates for estimating and verifying visual

range as well as documenting the hazy condition of the atmosphere. We estimated the uncertainty in visual range to be half the difference in distance between adjacent targets.

DISCUSSION

Composition of Aerosols in Forested Areas: For the average compositional data reported in Table 2, the relative amounts of the elements and ions in aerosols measured in the Great Smoky and Abastumani Mountains were remarkably similar to those measured in the Shenandoah Valley. For example, in the fine fractions, the sulfur for the three forested sites was in the form of sulfate and represented approximately 50% of the fine particle mass. Total carbon was the next largest component present in the fine fraction which was as follows: 15%, Great Smoky Mountains; 5.9%, Shenandoah Valley and 24%, Abastumani Mountains.

Figure 2 is a time series plot showing the concentrations of several species measured at Shenandoah Valley. Sulfate is plotted as ammonium sulfate since that is the result that would be obtained if the collected samples are not protected from neutralization by ambient ammonia. However, for our samples that were protected from neutralization after sampling, the actual molar concentrations for H^+ and NH_4^+ are shown in Fig. 3. It is apparent that during certain daytime sampling periods at both sites, H^+ exceeded NH_4^+ molar concentration indicating the presence of both H_2SO_4 and NH_4HSO_4. Acidity measurements were made on the aerosols collected in the Abastumani site, but no acidity was detected. In all three studies, filters were stored in ammonia-free chambers after sampling, but we cannot exclude the possibility of

neutralization by ambient ammonia during sampling and during handling. Thus, our measured ammonium and hydrogen ion concentrations are upper and lower limits, respectively, for the true atmospheric values.

The coarse-particle mass, Table 2, averaged 23%, 27%, and 42% of the fine mass for Great Smoky Mountains, Shenandoah Valley and Abastumani Mountains, respectively. While the coarse particle masses were roughly equal at each of these sites, the fine mass in the remote site of Abastumani was smaller by a factor of approximately two. Even though the fine mass was significantly smaller in the Georgian SSR, ammonium sulfate represented 48% of the mass, which is comparable to the Great Smoky Mountains and Shenandoah Valley aerosol composition. Substantial amounts of manganese (Mn) occurred in both the fine and coarse particles collected in the Abastumani Mountains, but were extremely low in the Great Smoky Mountains and only trace amounts were present in the Shenandoah Valley aerosol. The Mn levels in the Abastumani fine fraction tended to increase when the air masses originated from the north. A ferro-manganese ore processing plant was 50 km north of Abastumani and its impact on the aerosol composition is discussed by Dzubay and Stevens (1983).

Carbon and $^{14}C/^{12}C$ Measurements: Recent comparisons of methods (Cadle et al., 1981) to measure elemental, total and volatile carbon content of aerosols indicate that procedures that depend on combustion or pyrolysis to convert the carbon species into methane followed by flame ionization measurement, may produce substantially different results, depending on the conditions for combustion. For example, to completely convert all the aerosol carbon on quartz filters requires a temperature of at least 850°C and the presence of oxygen in the helium carrier gas. Without oxygen, a substantial amount of elemental carbon will not be pyrolyzed and consequently not be measured.

The volatile carbon analysis of our Shenandoah Valley samples was conducted at 450°C in the presence of MnO_2 (Stevens et al., 1980). At the time we performed these measurements, we believed the lower temperature and MnO_2 catalyst would reduce charring, and thus provide more realistic volatile carbon measurements. However, recent experiments show that this method may have underestimated the volatile organic component and thus overestimated the elemental carbon content. Also, the carbon measurements had to be corrected for the carbon present in the blanks. Typically, the volatile carbon content in blank quartz filters increased from a normal value of 1.0 $\mu g\ cm^{-2}$, before being transported to the field, to 5 $\mu g\ cm^{-2}$ after returning to the laboratory. Blank corrections were further complicated by the variations in the amount of carbon present in blanks from comparable quartz filter sets. These difficulties occurred even though we carefully protected the quartz filters from contamination. Blank filters were held in the automatic Sierra sampler for ten days along with the sample filters before they were removed from the filter tray and stored at room temperature in sealed plastic zip-lok bags. Ion chromatographic analyses of blank quartz filters after being returned from the field revealed the presence of carbonate, formate amd acetate ions (Mulik, personal communication). Work is going on to determine the origin of these organic acids and quantify their effect on aerosol volatile carbon measurements. However, until sampling and analytical procedures are developed to compensate or correct for the presence of these species, total aerosol organic measurements should be interpreted with caution. [Huntzicker (Personal communication), Moyers (Personal communication) and Cadle (Personal communication) are also concerned with volatile carbon measurements by combustion procedures, and acknowledge that previously published volatile carbon measurements are uncertain due to sampling artifacts

and variations in blank determinations.] We consider this a crucial area for further research.

We attempted to determine the relative amounts of particulate carbon from contemporary and fossil fuel carbon combustion sources by means of data on the $^{14}C/^{12}C$ ratio. The distinction between the two types is possible because contemporary carbon contains ^{14}C but fossil fuel carbon is essentially devoid of ^{14}C (Cooper et al., 1981). $^{14}C/^{12}C$ measurements made from aerosols collected in the Abastumani Mountains and Shenandoah Valley indicated that the amounts of total carbon that were of a contemporary origin were 73 ± 6% and 90 ± 8%, respectively. Here the uncertainties only include counting statistics and background corrections and are discussed in detail by Currie (1982); these uncertainties do not include potentially large effects which are discussed below. The standard deviations which reflect the variability of the measurements over the periods of study were 13% and 19% for Abastumani and Shenandoah, respectively.

These ^{14}C measurements must be interpreted with caution for the following reasons. During the Shenandoah Valley study insect contamination of the quartz filters in the Bell-vol sampler occurred. Although efforts were made to remove the insects, some portions may have remained and could have contributed to the contemporary carbon values. Also, as stated above, our blank carbon values were substantial, and could also have contributed to the contemporary carbon. Currie (1982) found the blank carbon present in the quartz filters used in these studies was indistinguishable from contemporary carbon. In addition, the Abastumani hi-vol filter samples contained both fine and coarse particles. Recent work by Currie et al. (1983) has shown that most

of the coarse particle carbon (samples collected in Los Angeles) is of a contemporary origin, possibly pollen. Finally, the total carbon present in the fine aerosol from the Shenandoah Valley was relatively small and even though a majority may be of a contemporary origin, possibly natural hydrocarbons, the average contribution to the haze producing components was only 5.9%.

Size Distribution Results: The Shenandoah Valley micro-orifice impactor data were fitted with a log-normal distribution function using a procedure described by Hasan and Dzubay (1983). The resulting average values of the fine mode's mass median diameter were 0.25, 0.27, and 0.17 μm for mass, S, and Pb, respectively. There was no evidence of particle bounce effects or of the occurrence of a significant nuclei mode having a mass median diameter below 0.1 μm. From the fact that the mass median diameter for lead is about 35% below that for mass and sulfur, one can infer that the lead particles were of fairly recent origin and had little time to coagulate onto the older and larger sulfate-containing particles. On the other hand, the fact that the Br/Pb ratio is 0.16 suggests some reaction with acid aerosol had occurred. Otherwise, the Br/Pb ratio would have been 0.4, the value characteristic of fresh auto exhaust. We cannot, however, exclude the possibility that acid aerosol reaction occurred on the filter after collection. The highway 0.5 km west of our sampling site may have been the source of the lead aerosol. The diameters presented above have relative precisions of ± 10% or less; the overall accuracy is ± 40% owing to an uncertainty in the impactor stage calibration data. Thus, our result for the aerodynamic diameter of fine mode mass is 0.25 ± 0.1 μm and is comparable to the volume mean geometric diameter of 0.3 μm, which was measured at our site by Weiss et al. (1982) by means of an optical particle counter and an electrical mobility analyzer.

Mass-Visibility Relationships: Investigators have shown that the product of fine mode mass concentration (m_f) and visual range (V) is approximately a constant if light scattering by fine particles is the predominant component of light extinction (Lodge et al., 1981). Lodge et al. showed that

$$m_f V = 1.25 \text{ g/m}^2 \quad (1)$$

provided that the following conditions were satisfied: (1) light scattering and absorption by coarse particles and by atmospheric gases are negligible, (2) light absorption by particles is negligible, (3) the particles contain no volatile water, (4) the visual objects are black, (5) the observer's contrast detection threshold is 2%, and (6) the scattering coefficient per unit fine mass concentration is 3.1 m^2/g.

Some of these conditions were satisfied during our measurements in Shenandoah Valley. For example, we used a technique described earlier (Lewis, 1981; Dzubay et al., 1982) to estimate that coarse particles contribute less than 1% to the extinction coefficient. Also, the dark tree-covered mountain slopes are fairly good approximations to black objects on the horizon. On the other hand, the assumption that an observer routinely detects 2% contrasts may be overly optimistic; a value of 5.5% was determined for observations of reasonably dark objects at airports (Booker and Douglas, 1977). In addition, the scattering coefficient (b_{sp}) per unit mass concentration (m_f) measured at our study site was 4.2 m^2/g, (Weiss et al., 1982). Finally, data obtained at the Shenandoah site by Ferman et al. (1981) indicate that at 1100 hrs, when our measurements were made, volatile water on particles contributed about 10%, and under such conditions light scattering accounted for 87% of the

light-extinction coefficient. The above data can be summarized as follows:

$$b_{ext} V = - \ln (\varepsilon) \tag{2a}$$

$$m_f/b_{sp}(\text{heated air}) = 0.24 \pm 0.02 \text{ g/m}^2 \tag{2b}$$

$$b_{sp}(\text{heated air})/b_{sp}(\text{ambient air}) = 0.90 \pm 0.05 \tag{2c}$$

$$b_{sp}(\text{ambient air})/b_{ext} = 0.87 \pm 0.05 \tag{2d}$$

where b_{ext} is the light-extinction coefficient, and Σ is the minimum contrast detectable by the observer. The uncertainties shown in Eq. (2) are our estimates; uncertainties were not stated by Weiss et al. (1982) for the coefficient in (2b) or by Ferman et al. (1981) for the data that we used to construct (2c) and (2d). By taking the product of the four coefficients in Eq. (2) we obtain for midday in Shenandoah Valley

$$m_f V = 0.74 \pm 0.08 \text{ g/m}^2 \text{ for } \varepsilon = 0.02 \tag{3a}$$

and

$$m_f V = 0.54 \pm 0.06 \text{ g/m}^2 \text{ for } \varepsilon = 0.055 \tag{3b}$$

The uncertainties shown in (3) were obtained by propagating independently the errors shown in (2).

Our measured results for V, m_f and their products are shown in Table 3. The mean value and standard error (standard deviation/$\sqrt{N}$) are

$$\overline{m_f V} = 0.43 \pm 0.03 \text{ g/m}^2, \tag{4}$$

which agrees better with the estimate shown in Eq. (3b) than with the one shown in (3a). This suggests that the minimum contrast detectable by our observer was not $\varepsilon = 0.02$ but was at least 0.055. We further tested the reciprocal relationship indicated in Eqs. (1) and (4) by computing the

correlation coefficient between m_f and V^{-1}. The resulting value, 0.95 for 13 samples, indicates a highly significant relationship between fine particle mass concentration and visual range. The correlation coefficient for fine fraction sulfate vs. V^{-1} is 0.89, which also indicates a significant relationship.

During a recent study in Houston, TX, visual ranges measured at local airports were averaged over 12-h daytime periods that corresponded to mass measurements. The resulting average product was 0.30 ± 0.04 g/m^2 (Dzubay et al., 1982). The lower value for Houston may be attributed to the use of man-made structures as visibility targets in Houston. These were brighter and smaller than the forested mountains in Shenandoah Valley; such structures would be more difficult to perceive at great distances.

Table 3

Daytime Sulfur and Mass Concentration and Visual Range

Measured Shenandoah Valley During Summer 1980

Date	Fine Particles[a], μg/m³ $SO_4^=$	(m_f)	V[b](km)	$m_f V$ (g m^{-2})	Relative Humidity (%)
7/24	8.5	16.8	26 ± 4	0.437	57.8
25	14.1	28.4	16 ± 2	0.454	47
26	7.1	34.9	13 ± 2	0.454	52.5
27	9.2	16.2	16 ± 2	0.259	62.9
28	3.5	10.3	26 ± 4	0.268	50
29	20.4	39.1	16 ± 1	0.626	50
30	31.5	60.1	8 ± 1	0.481	58.7
31	35.3	69.2	8 ± 1	0.554	61
8/1	8.6	24.1	16 ± 2	0.386	46.4
2		24.1	c		63
3	11.3	30.8	13 ± 2	0.400	61
4	4.0	11.0	24 ± 4	0.264	63.7
5	5.5	17.4	26 ± 4	0.452	56
Mean	13.3	29.4	17	0.420	
Standard Deviation	10.5	18.0	6.7	0.114	

[a] Sampling periods were 0600 to 1800 EDT

[b] Visual range is based upon observer's determinations once per day between 1045 and 1140 EDT.

[c] Visual range was greater than 30 km, but could not be determined because there were insufficient distant targets.

The average of the measured visual ranges at midday in Shenandoah Valley was 17 km, which is only 8% of the 240 km that would be possible in pure air where the visual range is limited by Rayleigh scattering. This result, plus the fact that the optical effects due to coarse particles and NO_2 were negligible, leads one to conclude that over 90% of the visibility degradation in Shenandoah Valley was caused by fine particles. Because sulfate and its related cations (ammonium and hydrogen) account for 63% of the fine particle mass and a correlation coefficient of 0.89 exists between 1/V and sulfate, we must conclude that sulfate is a major cause of visibility degradation in Shenandoah Valley.

Receptor Modeling of Shenandoah Valley Aerosols Data Sets: As a first step in deducing the origins of the fine particles in Shenandoah Valley, we analyzed the concentrations of elemental species of fine particles by factor analysis. Such an analysis provides a means of identifying groups of elements whose concentrations vary similarly from sample to sample. The factor analysis was performed by using the BMDP computing package (Dixon and Brown, 1979). Every elemental or chemical variable whose average measurement uncertainty was less than 20% of the variables' mean value was included in the factor analysis. Even though Se and both elemental and total carbon had larger percent uncertainties (Table 2), they were also included because of their intrinsic interest. Table 4 gives the results obtained with the Shenandoah Valley data using all BMDP default options (initial factor extraction by principal components analysis, unity initial estimates of communalities, retention of all factors with eigenvalues $\geq$ 1, and varimax rotation). The 4-factor solution is seen to account for 89% of the total variance. Total mass, sulfur, sulfate, hydrogen ion, ammonium, total nitrate and selenium are seen

to have large loadings on the first factor. The second, third and fourth factors in Table 5 are strongly suggestive of wind blown dust, "carbon", and motor vehicle sources, respectively. Additional factor analysis solutions, with as many as six factors, were also investigated. In all cases the composition and loadings of the first factor were virtually unchanged.

The fact that mass, sulfur, sulfate, hydrogen ion, ammonium, total nitrate, and selenium are grouped by factor analysis into the same factor indicates that they vary similarly from sample to sample. Figure 4 shows time series plots for ammonium sulfate, selenium, and nitrate. The correlation coefficients for sulfate vs. selenium and sulfate vs. gaseous plus fine particle nitrate are 0.71 and 0.75, respectively, for these data. Such behavior would result if these species had a common source and dispersion behavior.

A number of observations point to coal combustion as the link between the similarly varying aerosol concentrations of selenium and sulfate measured in this experiment. These include emissions inventory estimates and previous experimental results. The former information includes the estimate that 62% of the anthropogenic selenium emitted into the atmosphere comes from coal burning (National Research Council, 1976). Also, an emissions inventory prepared by Klemm and Brennan (1981) for the year 1978 showed that coal combustion accounted for 61% of the SO_2 in the SURE region [SURE region includes the twelve most populated industrialized states east of the Mississippi River]. On the experimental side at least three studies are noteworthy. Wangen (1981) collected size fractionated aerosol particles downwind from a coal-fired power plant. Samples taken when ambient SO_2

concentrations were high (in the plume), were separated from those with low SO_2 concentrations (background). Wangen reports 10-fold greater Se concentrations in plume samples. Thurston et al. (1982) have examined the compositions of aerosol samples collected near Boston, MA and found correlations with 72 h back-trajectories of wind data; air masses from the Ohio Valley/Midwest are higher in particulate sulfur and selenium than those which passed over the Eastern Seaboard. Finally, the work of Shaw and Paur (1983) on measurements in the Ohio River Valley inferentially linked ambient concentrations of sulfur and selenium to emissions from coal combustion.

If it is accepted that coal combustion is the major underlying cause of the selenium-sulfate association, what can be said about the origin of the coal combustion emissions themselves? Here the answer supplied by the SURE emissions inventory (Klemm and Brennan, 1981) is unambiguous: 56% of the SO_2 emissions were due to major coal-burning utilities. In other words 56/61, or 92%, of the SO_2 due to coal combustion was estimated to come from utility plants.

It is worth emphasizing that the factor analysis of Table 4 shows total nitrate to be associated with the "coal combustion" factor rather than the "leaded gasoline combustion" factor, even though the SURE inventory (Klemm and Brennan, 1981) estimates 51% of the emissions of the nitrate precursor NO to come from transportation sources compared with 25% from coal combustion. We suggest two possible explanations for this: (1) the difference in transport and conversion potentials of ground level (transportation) vs. elemental (major utilities) sources of NO; (2) the highest density of transportation sources is downwind (the Eastern Seaboard) of the measured site. Our results

seem to be the first that have shown an association not only between fine particle sulfate and selenium, but with acidity and total nitrate as well.

CONCLUSIONS

For the limited data sets collected in the remote forested areas of the Great Smoky Mountains, Shenandoah Valley and Abastumani Mountains we observed that sulfate was the dominant fine particle species while aerosol carbon was a minor component of the total fine particle mass concentration. In the Shenandoah Valley we calculated that 90% of visibility degradation was caused by fine particles. Because sulfates account for 63% of the fine particle mass, we conclude sulfates were the major cause of the haze in the Shenandoah Valley.

Carbon-14 measurements made on aerosol carbon collected in the Shenandoah Valley and Abastumani Mountains indicate that most of the carbon derives from contemporary carbon sources. However, because of the large uncertainties in the blank carbon and the relatively low concentration of carbon present in the ambient air at these two forested sites, we recommend that the values reported in this paper be considered preliminary until improved sampling and analysis procedures are developed to validate our observations.

Factor analysis of the aerosols collected in the Shenandoah Valley implies for the first time that both the fine-particle acid sulfates and nitrates are from a common source, and that the source appears to be coal-fired power plants, because of the additional correlation with selenium and the consistency with emission inventories.

Table 4

Factor Analysis Loading and Source Attribution of Chemical Species Present in Fine Particles Collected in the Shenandoah Valley Summer, 1980

	Factor Analysis Loading[a]			
VARIABLE	1	2	3	4
SOURCE ASSIGNMENT	COAL FIRED POWER PLANTS	SOIL	CARBON	COMBUSTION OF LEADED GASOLINE
$SO_4^=$	0.96	0.00	0.00	0.00
S	0.96	0.00	0.00	0.00
Mass	0.96	0.00	0.00	0.00
H^+	0.96	0.00	0.00	0.00
NH_4^+	0.83	0.00	0.00	0.00
NO_3^- Total	0.83	0.00	0.00	0.00
Se	0.80	0.00	0.00	0.00
Fe	0.00	0.95	0.00	0.00
Si	0.00	0.95	0.00	0.00
Ca	0.00	0.94	0.00	0.00
K	0.00	0.88	0.00	0.00
C Elemental	0.00	0.00	0.93	0.00
C Total	0.00	0.00	0.91	0.00
Pb	0.00	0.00	0.00	0.85
Br	0.00	0.00	0.00	0.80
Zn	0.00	0.00	0.00	0.69
% Fraction of Variance	40%	22%	14%	13%

[a] Loadings less than 0.500 replaced by zero

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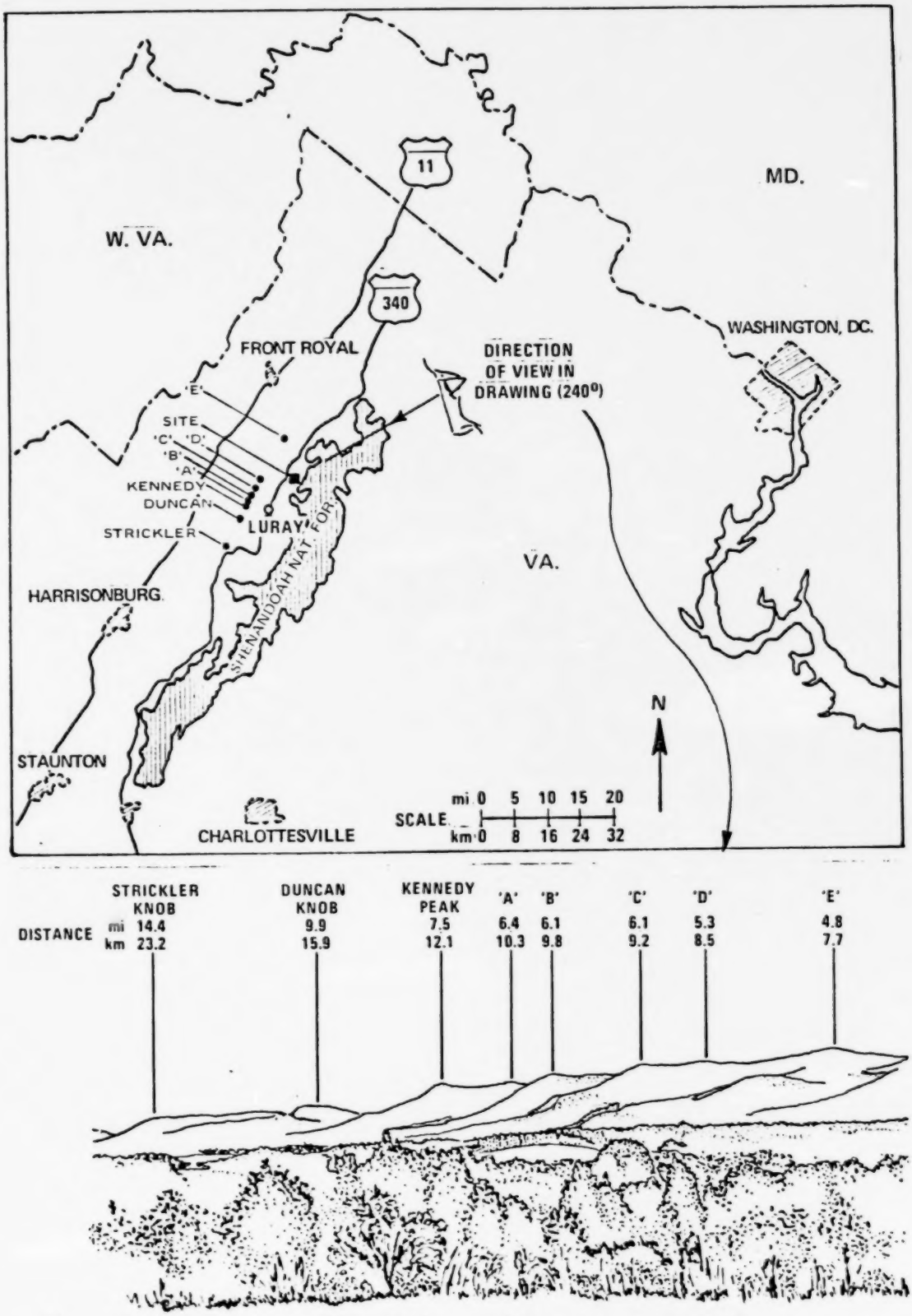
Figures

Figure 1. Shenandoah Valley field sampling site showing the scenic vista used in visibility observations.

Figure 2. Time series plot of mass, ammonium sulfate, carbon concentrations observed in the Shenandoah Valley between July 23 and August 6, 1980.

Figure 3. Time series plot of H^+ and NH_4^+ molar concentrations for aerosols collected in the Great Smoky Mountains and Shenandoah Valley. The dark places on the abscissa indicate nighttime sampling periods.

Figure 4. Time series plot of fine particle concentrations of ammonium sulfate, selenium and total fine nitrate (NO_3^- + HNO_3) collected in the Shenandoah Valley.



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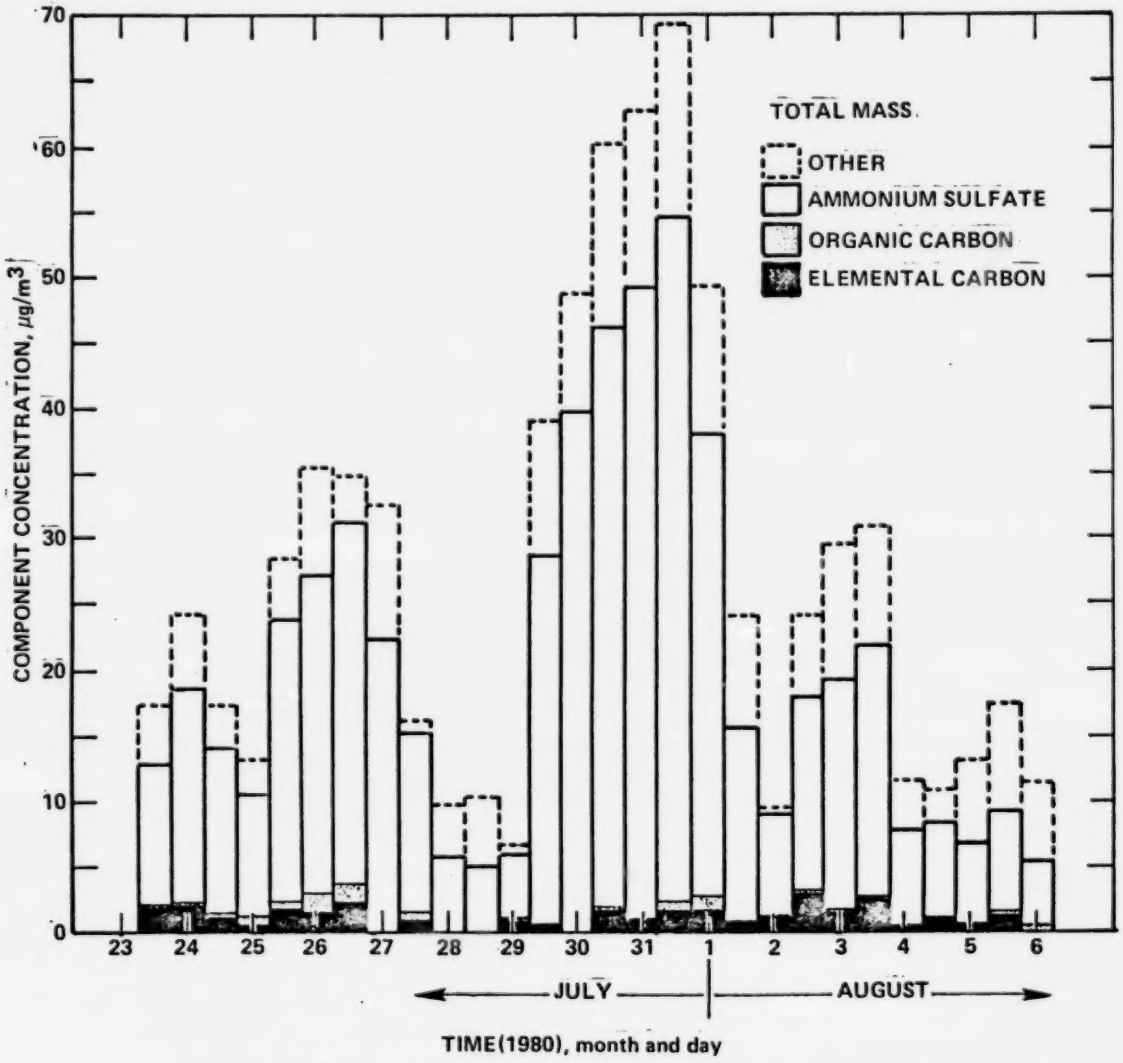
TIME SERIES PLOT OF AEROSOL COMPOSITION IN SHENANDOAH VALLEY, VA, JULY AND AUGUST, 1980



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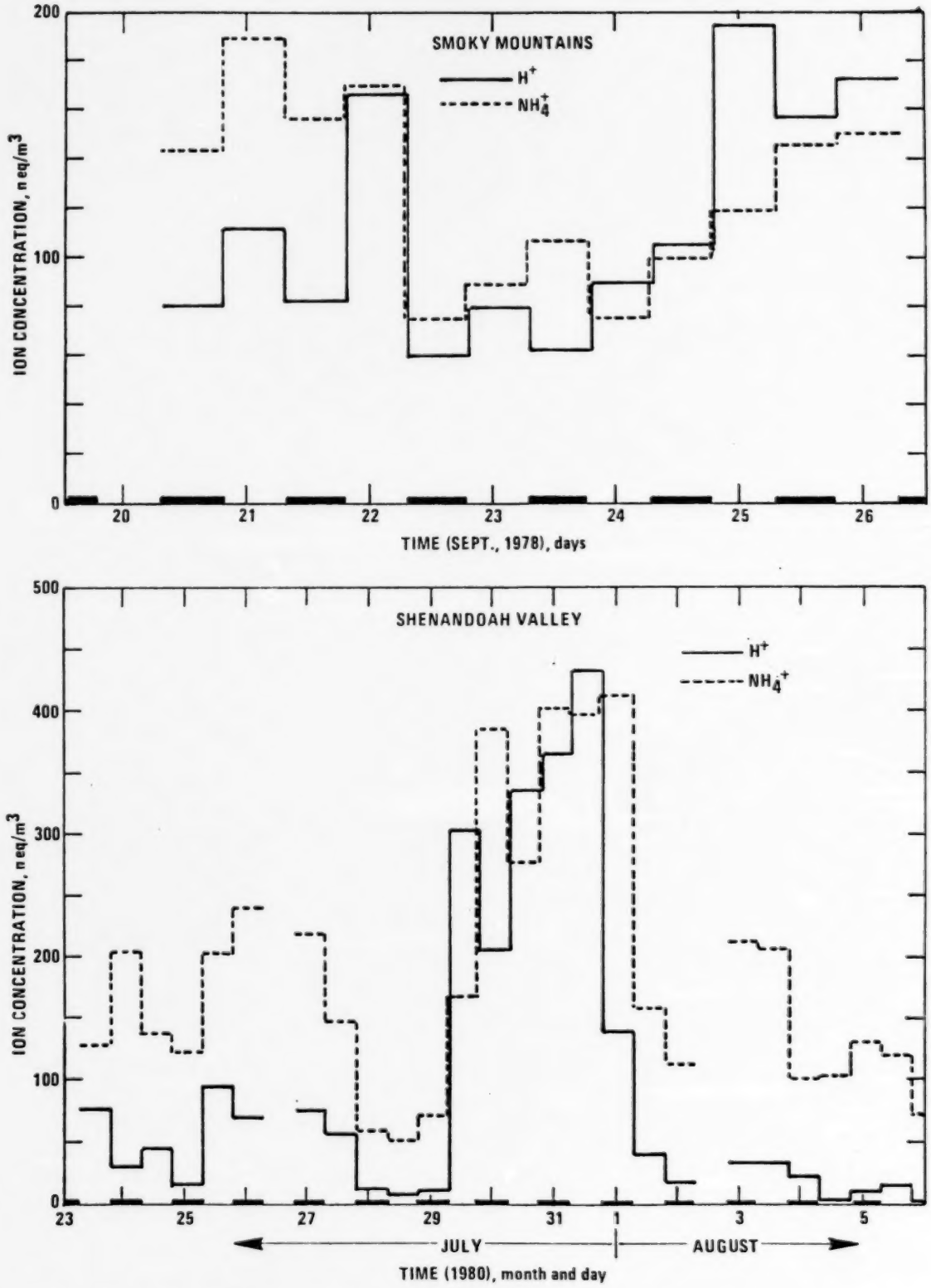

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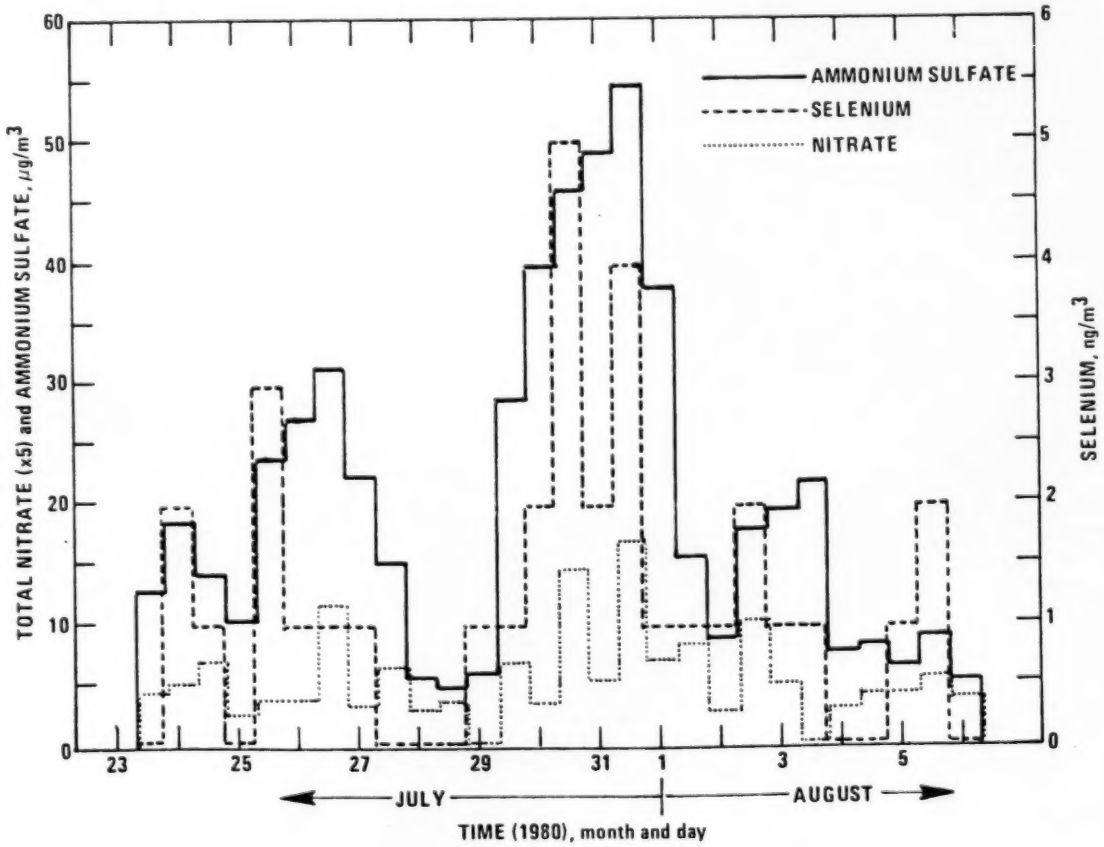
TIME SERIES PLOT OF NITRATE, AMMONIUM SULFATE, AND SELENIUM AEROSOL COMPOSITION IN SHENANDOAH VALLEY, VA, JULY AND AUGUST, 1980



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